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Extraction of Carbon Dioxide from Seawater by Ion Exchange Resin Part II: Using Strong Base Anion Exchange Resin

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14. ABSTRACT

Strong base anion exchange resins were studied to determine if they could be used as a feasible and practical method for sequestering carbon dioxide from seawater for use as a carbon feedstock in a sea-based fuel production process. Static and dynamic flow experiments to determine the resin bicarbonate and chloride selectivity and the effect of ionic strength on bicarbonate selectivity and capacity are reported. These data are used to determine the scaled up feasibility of a carbon capture process by this approach.

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EXTRACTION OF CARBON DIOXIDE FROM SEAWATER BY ION EXCHANGE RESIN PART II: USING STRONG BASE ANION EXCHANGE RESIN

1.0 BACKGROUND

The Ocean Thermal Energy Conversion (OTEC) process converts solar thermal energy absorbed by the ocean into electrical power [1,2]. During the OTEC process dissolved carbon dioxide (CO_2) in ocean water is liberated as a gas. Since CO_2 is implicated in climate change, there is significant interest in harvesting the CO_2 generated from the OTEC process and using it as a potential carbon source for the production of synthetic liquid hydrocarbon fuel (Synfuel) [3].

The CO_2 content liberated from ocean water by the OTEC process is actually only 2 to 3% of the total CO_2 available from ocean water. The remainder of this CO_2 is bound as dissolved bicarbonate [4]. The concentration of bound and dissolved CO_2 in the ocean is about 140 times greater than that found in air on a (w/v) basis [3]. Thus if processes are developed to take advantage of the higher concentration of CO_2 in ocean water coupled with the OTEC process, the overall process efficiency would be significantly improved, and there by greatly increasing Synfuel production.

A large ship with a 100 megawatt (MW) OTEC plant removes the heat energy content from 8.4 billion gallons of seawater per day [1,2]. Thus it can be envisioned that 32,000 to 48,000 m^3/day of carbon from CO_2 is available from the OTEC process itself and we propose additional processes to remove the remaining 97% to 98% bound as bicarbonate. These processes would take advantage of the ocean water already being pumped for the OTEC heat removal, thus for each gallon of water pumped the heat energy and the total carbon will be removed at the same time. This would result in 1.6 million m^3/day of CO_2 for producing Synfuel. A 100 MW OTEC plant would be capable of supplying enough electricity to generate hydrogen through commercial off the shelf conventional electrolysis equipment to produced 43,000 gallons of synfuel using a gas to liquids catalytic process.

Fuel is produced by combining the hydrogen and CO_2 in a gas to liquid scheme that is significantly different than that used by the Germans in WWII and currently used by Sasol in South Africa and Shell Oil in Malaysia [5,6]. These commercial processes rely on petroleum derived fossil fuels and they are not CO_2 neutral. In the process of integrating solar OTEC with CO_2 capture and utilization technologies, the principle carbon source for hydrocarbon production would be CO_2 from the ocean. In effect the process is CO_2 neutral and also eliminates the emission of sulfur and nitrogen compounds that are produced from the combustion of petroleum derived fossil fuel. In addition the process is advantageous in that it is independent of fossil fuels, foreign or domestic.

2.0 INTRODUCTION

Before a sea-based synthetic fuel process that combines solar OTEC with CO_2 capture can be envisioned, efficient and economical techniques for extracting large quantities of CO_2 (443,900 m^3/day for a 100,000 gallon fuel per day process aboard a platform) from seawater must be developed [7-9]. Near the ocean's surface (pH = 7.8) the total carbon dioxide content $[CO_2]_T$ is about 2,000 µmoles/kg. At all depths below 300 meters this concentration increases to 2,400 µmoles/kg [10,11]. This equates to approximately 100 mg/L of $[CO_2]_T$. The $[CO_2]_T$, as shown in equation 1 is the sum of the concentration of dissolved gaseous CO_2, bicarbonate, and carbonate.

$$\Sigma\ [CO_2]_T = [CO_2(aq)] +\ [HCO_3^-(aq)] + [CO_3^{2-}(aq)] \tag{1}$$

Approximately 2 to 3% of the CO_2 is in the form of a dissolved gas and the remaining 97 to 98% is in the chemically bound state as bicarbonate and carbonate. The concentration of $[CO_2]_T$ in air is 370 ppm (v/v) and this is only 0.7 mg/L on a (w/v) compared to the 100 mg/L in the ocean. Therefore it is readily apparent that the concentration of CO_2 in seawater is about 140 times greater than air [3].

To increase the rate and yield of carbon dioxide recovery from the sea, Hardy et al. investigated the use of a simple strong cation exchange resin system [7]. Johnson et al. showed that when the pH of seawater is decreased to 6 or less, the total CO_2 exists only in the dissolved gas form [12]. The ion exchange system successfully acidified seawater below pH 6 and subsequently the spent ion exchange resin was regenerated using deionized water instead of a strong acid. The volume of water per unit weight of resin required to regenerate the resin was much larger than the volume of CO_2 recovered, and potentially larger than the volume of fuel produced from that CO_2, and so this approach was deemed impractical [7]. Thus as one further avenue of exploration to increase carbon yield from the sea, strong base anion exchange resins are being investigated. It is well known that these resins work on the principle of exchanging hydroxide ions for anions in solution. Ion exchange resins offer several advantages for this particular application, because in general they are inexpensive, durable, and can be operated at high flow rates in various water media. In addition the selectivity of the resin can be tailored by using mixed beds or specific functionalized groups upon resin synthesis. Previous work conducted by Dorchak et al. demonstrated the ability of anion exchange resins to regenerate ammonia from ammonium bicarbonate [13]. Ammonia was being used as a solvent to capture CO_2 from flue gas. Schallcross et al. have demonstrated the ability to selectively extract gold cyanide complexes from water solutions containing 0 to 3 Molar KCl using strong base anion exchange resins [14]. In this work, static and dynamic flow experiments were conducted using strong base anion exchange resins. The resin bicarbonate and chloride selectivity and the effect ionic strength has on bicarbonate selectivity and capacity are discussed. These data are used to determine a scaled up carbon capture process by this method.

3.0 EXPERIMENTAL

Ion exchange resins were obtained from Sigma Aldrich Chemical Co. Two of the resins were both Amberjet 4400 strongly basic anion exchangers. One was in the in the hydroxide form and the other in the chloride form. The other resin was Ambersep 900 in the hydroxide form. In each experiment the resins were used without pretreatment. The chemicals ($NaHCO_3$ and $NaCl$) utilized in these studies were of reagent grade, and the dionized water was obtained on site and used for all experiments. The Amberjet resins were challenged in static experiments using 0.0015, 0.0023, 0.005 Molar $NaHCO_3$. A 0.00034 M solution of $NaHCO_3$ was used in the static experiments with Amberjet 4400 in the hydroxide form to determine the effect chloride concentration has on bicarbonate selectivity. Chloride was added as $NaCl$ in increments equivalent to 33%, 67%, and 100% of the concentrations (19.4 g/L) found in seawater.

For each of the static experiments, a 15 mL aliquot of a known bicarbonate solution was measured by a UIC Coulometric system (UIC Inc, Joilet, IL 60436) to verify the target values of CO_2 for that solution [12]. Then 500 mL of that solution was contacted with 0.5 gram of fresh resin, and stirred continuously. A 15 mL aliquot was collected and measured by the coulometer at each time interval given in Table 1 to determine the CO_2 extracted from the solution by the resin in the form of bicarbonate. After the experiment the solution was decanted from the resin and the CO_2 content of the recovered spent resin was measured by the coulometer. Table 2 shows the average CO_2 measured on the resin before and after contact with the bicarbonate solution. All solutions for the coulometer were of reagent grade and purchased from UIC Inc.

Stationary column dynamic flow experiments to determine CO_2 (bicarbonate) capacity were conducted with individual columns of Amberjet 4400 in the hydroxide form and Ambersep 900 in the hydroxide form. For each of the experiments, 12 grams of resin were packed into a 20 mL plastic syringe (tube length 9.4 cm and diameter 2.0 cm). The resin beads are spherical (about 0.7 mm diameter) and were retained in the column by a cotton mesh or a stainless steel mesh. Each column was attached to a pump using Teflon tubing so that water could be pumped through the column at 7 to 10 mL/min. The stainless steel single piston HPLC pump (Model 2350) was obtained by ISCO, Inc.

In the stationary column dynamic experiments to determine chloride competition, a fresh 12 gram column of resin was challenged with one of six different effluents (100% chloride (19.4 g/L), 75% chloride, 75%/25% chloride/bicarbonate, 50%/50% chloride/bicarbonate, 50% chloride, and Key West seawater). The chloride was added as $NaCl$ and the bicarbonate was added as $NaHCO_3$. As the effluent was passing over the column of the resin at approximately 7 mL/min, the pH of the effluent increased significantly, and as the resin became spent the pH decreased. Approximately 10 mL aliquots were collected and measured for chloride content by titrating each aliquot with a 0.1 M solution of $AgNO_3$ solution. The indicator used in the titrations was K_2CrO_4.

Three separate regeneration experiments were conducted. In the first set of experiments 12 g columns of Amberjet 4400 and Ambersep 900 were challenged with 48 mL of a 50%/50% chloride bicarbonate solution. A 100 mL of 80 °C deionized water was passed over each resin

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bed and collected for coulometric analysis. The 100 mL hot water rinse was repeated for each column and analyzed.

In the second set of regeneration experiments, a 12 gram column of Amberjet 4400 was challenged with 38 mL of Key West seawater. To regenerate the resin, a total of 33 mL of 60 °C water was added to the resin bed in three separate increments of 10 to 12 mL. Each increment was in contact with the resin bed for 2 minutes. A total volume of 33 mL was collected for analysis of chloride content. This procedure was repeated an additional 2 times such that 3 separate samples containing 33 mL of solution were collected and analyzed for chloride content.

In the final regeneration process a 12 gram column of Amberjet 4400 was challenged with 38 mL of Key West seawater. The column was rinsed with 100 mL of 60 °C water and approximately 10 mL aliquots of the effluent were collected and analyzed for chloride content.

4.0 RESULTS

4.1 Static Experiments

To begin to understand the feasibility of using strong base anion exchange resins to capture total CO_2 from seawater, simple model solutions of sodium bicarbonate and sodium bicarbonate/sodium chloride were used to challenge the resins. In deionized water the bicarbonate species forms a basic solution as shown in the following equation 1.

$$NaHCO_3 + H_2O \rightleftharpoons NaOH + H_2CO_3 \qquad (1)$$
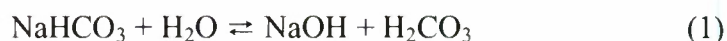
When the sodium bicarbonate influent contacts a strong base anion exchange resin in the hydroxide form, the carbonic acid disproportionates to bicarbonate and water as shown in equation 2.

$$H_2CO_3 + OH^- \rightleftharpoons HCO_3^- + H_2O \qquad (2)$$
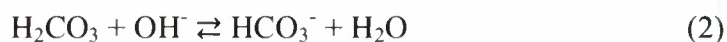
When the sodium bicarbonate influent contacts a strong base anion exchange resin in the chloride form, the carbonic acid disproportionates to bicarbonate and hydrochloric acid as shown in equation 3.

$$H_2CO_3 + Cl^- \rightleftharpoons HCO_3^- + HCl \qquad (3)$$

Both the loss in CO_2 in the form of bicarbonate in the influent to the resin and the resin uptake of CO_2 in the form of bicarbonate from the influent are measured by coulometery by difference. Initial static experiments were conducted with sodium bicarbonate and sodium chloride because these experiments are a quick simple method of determining the rate of exchange of ions by

sampling the solution at intervals. These experiments can show different rates of exchange for different ion systems. The factors that influence the rate of resin exchange are resin particle size, efficient mixing of resin and solution, concentration of solution, and solution temperature [15].

4.1.1 Amberjet 4400 in OH Form Experiments

Table 1 provides a summary of the solutions used to challenge the strong anion exchange resin as a function of time. Experiments were initially conducted using a 0.0015 M bicarbonate solution because this concentration is roughly half that found in seawater (100 mg/L). After the 0.0015 M solution is contacted with 0.5 gram of resin for 30 minutes, the CO_2 content of the bicarbonate solution is reduced by 52%. Once the resin has been in contact with the solution for 60 minutes, 70% of the CO_2 content appeared to be extracted by the resin.

Table 1 - The Solution Properties of Static Experiments Using Amberjet 4400 in OH Form

Sample Concentration (Molar)	Resin Exposure Time (minutes)	CO_2 Content Solution (mg/L)	CO_2 Content Solution (mg)	Reduction (%)
0.0015	0	0.051	26	0
0.0015	30	0.025	13	52
0.0015	60	0.016	8	69
0.0015	90	0.015	8	71
0.0015	120	0.015	8	70
0.0015	150	0.016	8	69
0.0023	0	0.101	51	0
0.0023	30	0.069	35	32
0.0023	60	0.068	34	33
0.0023	90	0.067	34	34
0.0023	120	0.069	35	32
0.0023	150	0.069	34	32
0.0050	0	0.220	110	0
0.0050	30	0.179	90	19
0.0050	60	0.179	90	19
0.0050	90	0.180	90	18
0.0050	120	0.181	91	18
0.0050	150	0.180	90	18
0.0075	0	0.330	165	0.0
0.0075	30	0.285	143	14
0.0075	60	0.287	144	13
0.0075	90	0.286	143	13
0.0075	120	0.283	142	14
0.0075	150	0.285	143	14

In Table 2, the resin's initial CO_2 content directly from the bottle measured 1 mg/0.5 gram of resin. After the resin was in contact with a 0.0015 M bicarbonate solution for 150 minutes, the resin was sacrificed. The results in Table 2 show that 19 mg of CO_2 was measured on the 0.5 gram of resin as well as the 1 mg/0.5 gram of initial CO_2 found on the resin taken from the bottle. This agrees with the results from the solution which indicated that 18 mg of CO_2 was extracted from the solution after 150 minutes (Table 1). In addition, the resin extracts much of the CO_2 within the first 30 minutes as illustrated in Figure 1.

Table 2 - Resin Properties of Static Experiments Using Amberjet 4400 in OH Form (150 minute contact time).

Sample Concentration (Molar)	Total mg CO_2 in 500mL sample	Total mg CO_2 extracted from solution	Total mg CO_2 extracted on 0.5 gram resin
0	0	0	1 (initial)
0.0015	26	18	19
0.0023	51	17	19
0.0050	110	20	24
0.0075	165	22	24

When the bicarbonate concentration was increased to a concentration more equivalent to that found in seawater (0.0023 Molar), the CO_2 content of the solution was reduced by over 30% in 30 minutes. The CO_2 content found on the resin in Table 2 was 19 mg for 0.5 gram of resin. This is the equivalent to the amount extracted by the resin when it was exposed to a 0.0015 M bicarbonate solution. This suggests that the resin capacity will be reached at concentrations of bicarbonate that are found in seawater.

To challenge the resin further and see if the CO_2 equilibrium could be shifted such that more CO_2 would be extracted onto a half of a gram of resin, the bicarbonate concentration was increased to 0.005 Molar. The results in Tables 1 and 2, show that the capacity of the resin was reached within 30 minutes and approximately 5 mg of additional CO_2 was extracted onto the resin (24 mg). However, when the bicarbonate solution was tested, only a loss of an additional 1 mg of CO_2 was measured.
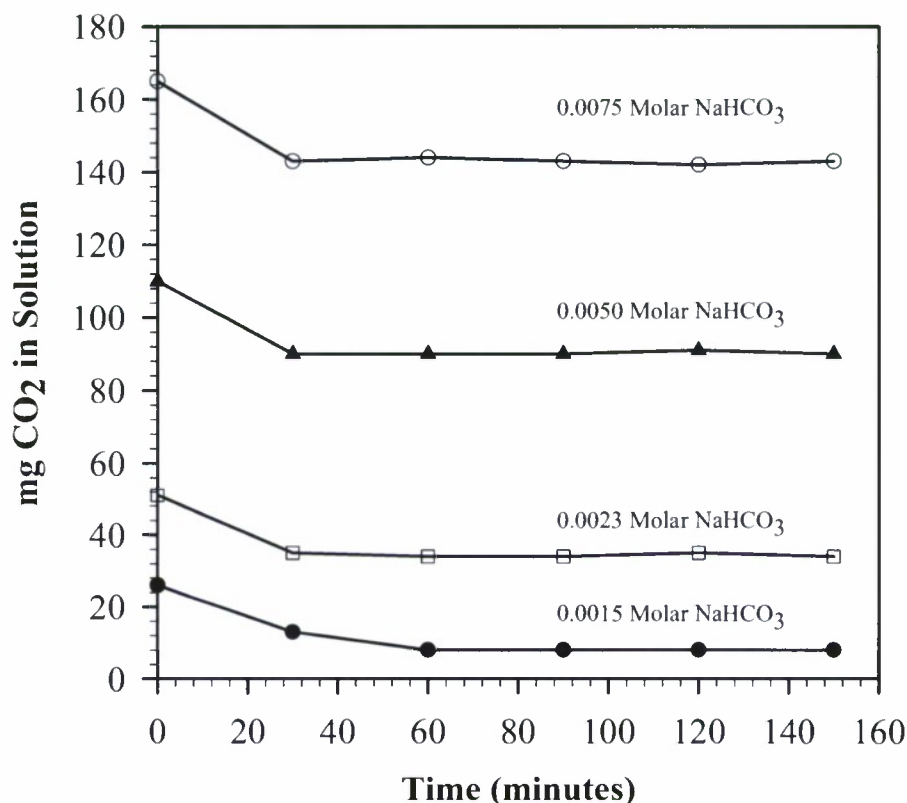
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Figure 1 - CO_2 Extraction on 0.5 g of Amberjet 4400 Strong Base in the OH Form

The increase in CO_2 content found on the resin after increasing the bicarbonate concentration to 0.005 Molar prompted testing the resin's performance in a 0.0075 Molar solution of bicarbonate that contained approximately 165 mg of CO_2. Table 2 shows that once again 24 mg of CO_2 was extracted from the bicarbonate solution onto the resin in the same time interval. Under these conditions, the bicarbonate solution showed only a loss of 22 mg of CO_2. The small discrepancies in the mass balance between the bicarbonate solutions and the resin are within the error limits of the coulometer and may also be attributed to re-equilibration of CO_2 in the solution with air over the long time intervals studied.

In efforts to understand the effect ionic strength has on bicarbonate selectivity of the resins, 0.5 gram of Amberjet 4400 in the hydroxide form was challenged with 0.00034 Molar $NaHCO_3$ and increasing concentrations of Cl^- ion. Chloride was added as NaCl in increments equivalent to 33%, 67%, and 100% of the concentrations (19.4 g/L) found in seawater. Figure 2 shows that after the resin is in contact with a 0.00034 M $NaHCO_3$ solution for 65 minutes, the CO_2 content of the solution is reduced approximately 64%. When chloride was added to the solution in 33%, 67%, and 100% concentrations of those found in seawater, the CO_2 content of the water appears to rise. This increase in CO_2 content is attributed to the exchange of Cl^- ions with the HCO_3^- ions that are initially measured on the resin when it comes straight from the bottle.
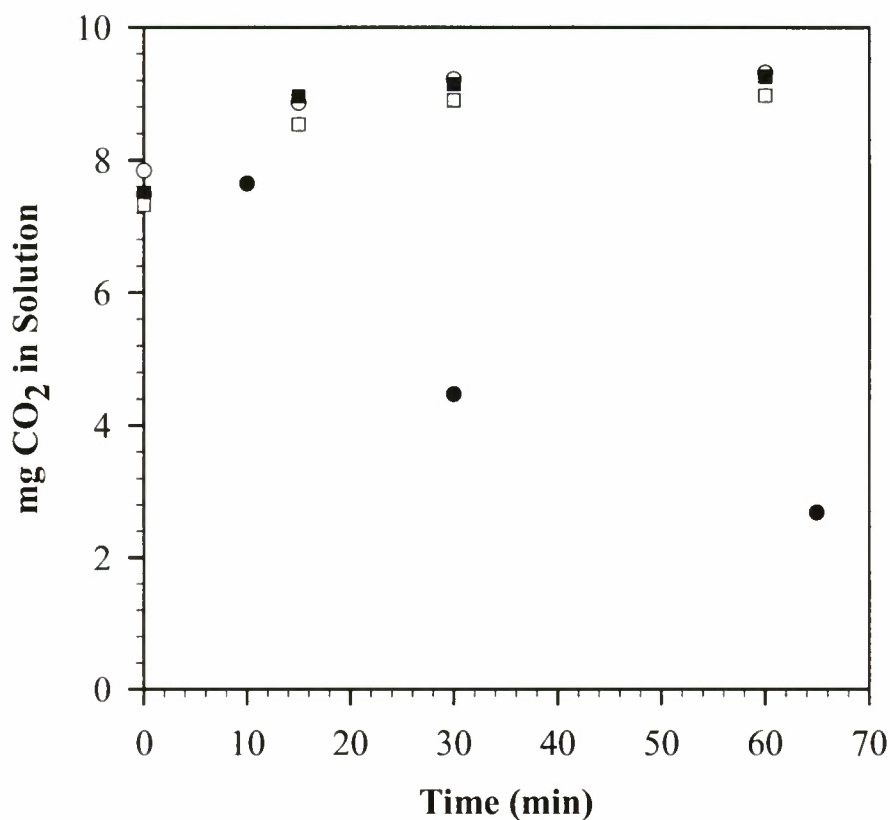
Figure 2 - Effect of Ionic Strength on CO_2 Extraction Using 0.5 g of Amberjet 4400 Strong Base in the OH Form [(●) 0.00034 M $NaHCO_3$ (○) 0.00034 M $NaHCO_3$ and 33% NaCl, (■) 0.00034 M $NaHCO_3$ and 67% NaCl, (□).00034 M $NaHCO_3$ and 100% NaCl.

4.1.2 Amberjet 4400 in Cl Form Experiments

Similar static experiments were conducted with a 0.5 gram of the chloride form of the resin and a summary of the results are provided in Table 3. The Table indicates that the resin's initial CO_2 content from the bottle measures 0.6 mg/0.5 gram of resin. At bicarbonate concentrations equivalent and lower to those found in seawater (0.00115 and 0.0023 M), this resin takes 30 minutes longer to reach equilibrium with the bicarbonate solution.

Table 4 shows that at theses concentrations only 11 and 16.4 mg of CO_2 were extracted onto the resin. This is significantly less than the 19 mg extracted by the hydroxide form of the resin. However, at higher bicarbonate concentrations (0.005 and 0.0075) the Cl form of the resin extracts as much and more CO_2 25.4 mg and 27.4 mg. In addition the Cl from of the resin at these concentrations never appears to reach its full capacity.

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Table 3 - The Solution Properties of Static Experiments Using Amberjet 4400 in Cl Form

Sample Concentration (Molar)	Resin Exposure Time (minutes)	CO_2 Content Solution (mg /L)	CO_2 Content Solution (mg)	Reduction (%)
0.0015	0	0.051	26	0.0
0.0015	30	0.033	17	35.1
0.0015	60	0.029	15	42.7
0.0015	90	0.028	14	45.2
0.0015	120	0.027	14	46.1
0.0015	150	0.027	14	46.4
0.0023	0	0.101	51	0.0
0.0023	30	0.069	35	32.1
0.0023	60	0.064	32	36.4
0.0023	90	0.063	32	37.3
0.0023	120	0.062	31	38.2
0.0023	150	0.060	30	40.7
0.0050	0	0.220	110	0.0
0.0050	30	0.171	86	22.3
0.0050	60	0.167	84	24.0
0.0050	90	0.168	84	23.6
0.0050	120	0.168	84	23.5
0.0050	150	0.168	84	23.8
0.0075	0	0.330	165	0.0
0.0075	30	0.273	137	17.3
0.0075	60	0.272	136	17.7
0.0075	90	0.271	136	17.9
0.0075	150	0.267	134	19.0

Table 4 - Resin Properties of Static Experiments Using Amberjet 4400 in Cl Form (150 minute contact time).

Sample Concentration (Molar)	Total mg CO_2 500 mL sample	Total mg CO_2 extracted from solution	Total mg CO_2 extracted on 0.5 gram resin
0	0	0	(initial) 0.6
0.0015	26	12	11
0.0023	51	21	16
0.0050	110	26	25
0.0075	165	31	27

4.2 Stationary Column Dynamic Flow Experiments

Though static experiments provide rate exchange information for different ions, the most practical method of operating ion exchange resins is flowing influent through a stationary phase column. This also maximizes exchange efficiency. In this particular application, exchange efficiency is important when the targeted anion HCO_3^- is 240 times less concentrated than the competing anion Cl^- [15].

4.2.1 Amberjet 4400 in OH Form Experiments

Table 5 provides a summary of the solutions used to challenge the strong anion exchange resin as a function of chloride and bicarbonate concentration. The objective of these experiments was to establish how much chloride ion could be extracted on to the column before breakthrough and the extent to which bicarbonate competed with chloride for active sites on the resin.

All experiments were conducted using a freshly packed 12 gram resin bed. In each experiment the influent was passed over the column at approximately 7 mL/min and approximately 10 mL aliquot samples were collected and measured for chloride content. Figure 3 illustrates the grams/L of chloride measured as a function of specific volume of aliquot collected after contact with the resin bed. For a solution containing 9.7 g/L of chloride (50% of the seawater chloride concentration), the chloride begins to break through the column once 58 mL of influent has passed over the column. It takes an additional 50 mL before the column is completely exhausted and the chloride concentration (9.7 g/L) of the effluent reaches that of the initial influent before contact with the resin.

Table 5 - Breakthrough Properties of Chloride Using Amberjet 4400 in OH Form

Solution	Solution Concentration (g/L)	Breakthrough (mL)	Inflection point (mL)	Chloride Capacity (mg/g)
50% Chloride	9.7	58	78	47
50% Chloride 50% Bicarbonate	19.4	38	66	31
75% Chloride	14.5	38	56	46
75% Chloride 25% Bicarbonate	19.4	38	49	46
100% Chloride	19.4	38	47	61
Key West Seawater	21	28	38	49
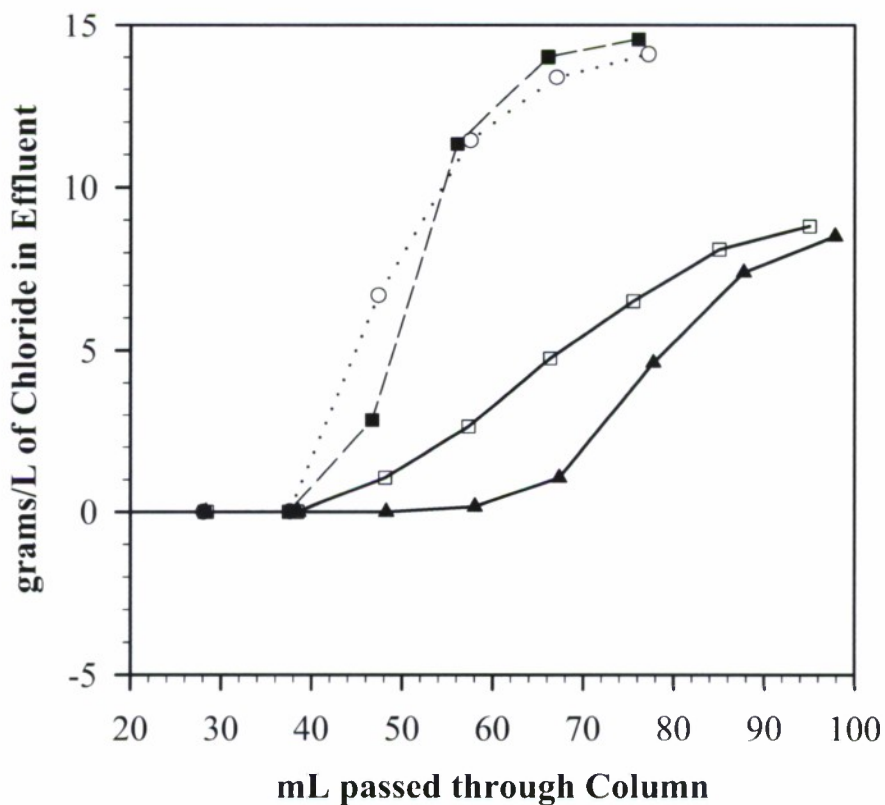
Figure 3 - Chloride Breakthrough Curves for 12 grams of Amberjet 4400 Strong Base in the OH Form at a Flow rate of 7 to 10 mL/min [(…○…) 75%/25% Chloride/Bicarbonate, (−−■−−) 75% Chloride, (-□-) 50%/50% Chloride/Bicarbonate, (▲) 50% Chloride].

When the resin was challenged with a 50%/50% mixture of bicarbonate to chloride anions at a total ion concentration of 19.4 g/L, chloride breakthrough begins to occur after 38 mL of influent has passed over the column. The breakthrough curve has also shifted significantly to the left from that produced by a 50% chloride solution. This implies that the bicarbonate anion is competing for the active sites on the resin causing the chloride anion to break through earlier. Additional evidence to support anion competition is shown by the difference between the breakthrough curves for a 75% chloride solution (14.55 g/L) and a 75%/25% chloride bicarbonate solution (19.4 g/L). The chloride breaks through for both curves after 38 mL of influent have passed over the column, however the 75%/25% curve is shifted further to the left. The shift is not as significant as the one that occurs between a 50% chloride solution and a 50%/50% bicarbonate chloride solution because there is less competition with bicarbonate as the ratio of chloride to bicarbonate increases.

For each solution used to challenge the resin, the derivative of the chloride breakthrough curves was taken and the inflection points are given in Table 5. The Table shows the inflection point decreases with increasing chloride concentration from 50% to 100%. Furthermore, as the chloride ratio to bicarbonate increases from 50% to 75% the inflection point decreases. Thus the trends highlight and differentiate between the effects of anion concentration and competition on chloride breakthrough.

With respect to resin capacity, the breakthrough curves and the inflection points illustrate how capacity changes with concentration as the static experiments suggested. When the resin was challenged at the lower chloride concentration (50%), the measured capacity of the resin is 47 mg/gram of resin. This result is similar to that achieved for the highest bicarbonate concentration used to challenge the resin in the static experiments (Table 2). When the concentration was increased to 19.4 grams of chloride, the exchange equilibrium is shifted such that more chloride is extracted onto the resin and a capacity of 61 mg/g of resin was measured for chloride.

Key West seawater was used to challenge the resin in order to simulate sample conditions that would be encountered in an actual ocean process for sequestering CO_2. The measured chloride concentration of this sample was 21 g/L. Table 5 shows breakthrough occurred quicker for this solution (28 mL). This is explained by the higher concentration of chloride in the seawater and the additional competition that arises from the sulfate anions present in the seawater. The additional anion competition is likely responsible for the 20% reduction in capacity when compared to the 100% chloride solution.

To understand and quantify the behavior of bicarbonate in the presence of large concentrations of chloride, CO_2 breakthrough was monitored for both a 50%/50% bicarbonate chloride solution and a Key West seawater sample. The results are summarized in Tables 6 and 7. The initial CO_2 concentration of the 50%/50% bicarbonate chloride solution used as the influent to challenge a 12 gram resin bed was 8.38 mg/mL. After the first 9.5 mL of influent containing 78.77 mg of CO_2 contacted the resin bed, the CO_2 content of effluent collected measured 1.33 mg. Though CO_2 breakthrough occurs significantly sooner than chloride breakthrough (38 mL total), most of the CO_2 is extracted onto the resin. Table 6 shows the extraction of CO_2 continues to increase as the resin is challenged until the resin reaches a

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maximum capacity of 22.6 mg/gram between 38 and 48 mL of total challenge. The CO_2 capacity is 27% less than the chloride capacity (31 mg/g) for the same solution. Though these anions compete, it is clear the resin has a stronger preference for chloride anions.

Table 6 - Breakthrough Properties of CO_2 in 50%/50% Chloride Bicarbonate Solution Using Amberjet 4400 in OH Form

50/50 effluent (mL)	CO_2 in 50/50 effluent (mg)		CO_2 in 50/50 influent (mg)	CO_2 extracted from influent (mg)	Total CO_2 (mg/gram resin)
9.4	1.3		78.8	77.4	6.5
19.0	2.1		158.8	156.7	13.1
28.5	8.3		238.4	230.2	19.2
38.5	55.4		322.2	266.8	22.2
48.2	132.0		403.5	271.5	22.6
57.4	221.6		480.6	259.0	21.6
66.4	315.5		556.0	240.5	20.0
75.6	391.0		633.1	242.2	20.2
85.1	465.6		712.7	247.1	20.6
95.05	532.0		796.5	264.6	22.1

Table 7 - Breakthrough Properties of CO_2 in Key West Using Amberjet 4400 in OH Form

Seawater effluent (mL)	CO_2 in Seawater effluent (mg)		CO_2 in seawater influent (mg)	CO_2 extracted from influent (mg)	Total CO_2 (mg/gram resin)
9.5	0.5		1.0	0.5	0.04
19.1	1.1		1.9	0.8	0.07
28.5	4.0		2.9	-1.2	
38.0	7.9		3.8	-4.1	
47.5	10.1		4.8	-5.3	
56.9	11.7		5.7	-6.1	
75.9	14.4		7.6	-6.9	

The CO_2 capacity measured for a 50%/50% bicarbonate chloride solution, the results of the ionic strength static experiments, and the concentration of chloride in seawater suggest very little extraction of CO_2 will be possible from a seawater solution using these dynamic flow experimental conditions. To substantiate this, Key West seawater containing 0.100 mg/mL of CO_2 was used to challenge a 12 gram resin bed. From Table 7, the CO_2 content of the first 9.4 mL of effluent collected after contact with the 12 gram resin bed was 0.48 mg. Thus approximately 0.48 mg of CO_2 was collected on the column and CO_2 breakthrough occurred immediately. For the same solution, chloride breakthrough occurred after 28 mL. When a total of 28.5 mL of effluent was collected after passing through the column, the total CO_2 content of

the effluent measured 4 mg. Thus the effluent was approximately 1.4 times more concentrated than the initial influent solution. This increase in CO_2 content of the effluent implies that once the chloride has broken through it begins to exchange with the HCO_3^- ions that are on the resin and CO_2 is no longer extracted from the influent (Table 7 CO_2 extracted from influent becomes negative). Though the flow experiments were successful at increasing the exchange efficiency of bicarbonate in the presence of high chloride concentrations, the results verify those found for the ionic strength static experiments in that chloride anions will preferentially displace bicarbonate anions from the resin bed.

4.2.2 Ambersep 900 in OH Form Experiments

Ambersep 900 in the OH form is a macroporous type 1 strong base anion exchange resin. The pores in the resin structure are larger than those resins supplied as a gel (Amberjet 4400). Initially the exchange capacity of these resins may be less, however they are better equipped to handle harsh operating environments such as seawater. In addition the larger pores sizes may be better suited for the removal of bicarbonate as CO_2 using different regeneration processes.

Similar solutions shown in Table 5 were used to challenge Ambersep 900. Table 8 provides a summary of the breakthrough results. From the Table, the chloride capacity of the resin appears to be very similar to that of Amberjet 4400 at the higher concentrations of chloride and bicarbonate. In addition the competition at higher chloride bicarbonate concentrations was comparable as shown by the inflection points obtained by the derivatives of the breakthrough curves. Similar capacity and exchange efficiencies obtained for Ambersep 900 suggest there is no significant advantage in resin performance over that of Amberjet 4400.

Table 8 - Breakthrough Properties of Chloride Using Ambersep 900 in OH Form

Solution	Solution Concentration (g/L)	Breakthrough (mL)	Inflection point (mL)	Capacity (mg/g)
50% Chloride	9.7	38	66	31
75% Chloride	14.5	38	57	46
75% Chloride 25% Bicarbonate	19.4	38	48	46
100% Chloride	19.4	38	48	61

4.3 Resin Regeneration

Once the bicarbonate ion has been extracted onto the resin and the resin is exhausted, the most effective method of regeneration is the use of a strong base such as sodium hydroxide. However these methods are not practical for any sea-based operation. One alternative approach for regeneration of anion exchange resin is by hot water. This method was demonstrated by Dorchak et al. in a process to regenerate ammonia from ammonium bicarbonate [13].

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4.3.1 Amberjet 4400 in OH Form-Bicarbonate Recovery

A 12 gram column of Amberjet 4400 was challenged with 48 mL of a 50%/50% chloride bicarbonate solution using gravity flow. To regenerate the resin a total of 100 mL of 80 °C deionized water was passed over the resin bed and collected for coulometric analysis. This procedure was repeated such that two 100 ml samples were collected and tested for CO_2 content. The CO_2 content of the first 100 mL aliquot measured 27 mg and the second 100 mL measured 1 mg. Since the CO_2 capacity for the resin is 22.6 mg/g of resin (Table 6) for this solution, than approximately 1/10 of the CO_2 on the resin was recovered. When 0.5 gram of the resin that was exposed to the hot water in an attempted regeneration was sacrificed for CO_2 content determination, the amount of CO_2 found on the resin sample was 7.5 mg. Thus it is estimated that 179 mg of CO_2 is still left on the column and 33% of the CO_2 was liberated from the resin by this method. It is important to note that 24 mg of the 179 mg is initial CO_2 found on the resin bed before contact with an influent. The discrepancy between the amount of CO_2 found in the rinse (80 °C water) and that found on the resin may be explained by the simple loss of CO_2 to the atmosphere at those water temperatures.

4.3.2 Ambersep 900 in OH Form-Bicarbonate Recovery

Ambersep 900 was challenged with the same 50%/50% chloride bicarbonate solution and regenerated using 80 °C deionized water. The CO_2 content of the first 100 mL measured 71 mg and an additional 1 mg was measured in the second 100 mL. When 0.5 gram of the resin was sacrificed, the amount of CO_2 found on the resin was 6.4 mg. Thus 154 mg of CO_2 is still left on the column and approximately 43% of the CO_2 was liberated from the resin. The static experiments and the stationary column dynamic experiments suggest that the CO_2 and Cl capacity of Ambersep 900 is similar to that of Amberjet 4400. Thus the 10% increase in the liberation of CO_2 by hot water observed using Ambersep 900 may be attributed to the larger pore sizes in the resin structure compared to that of Amberjet 4400. In addition, as observed for Amberjet 4400, the difference between the amount of CO_2 found in the rinse (80 °C water) and that found on the resin may be explained by the simple loss of CO_2 to the atmosphere at those water temperatures.

4.3.3 Amberjet 4400 in OH Form-Chloride Recovery

Additional studies were conducted to determine chloride recovery from Amberjet 4400 by hot water. A 12 gram column of Amberjet 4400 was challenged with 38 mL of Key West seawater. To regenerate the resin, a total of 33 mL of 60 °C water was added to the resin bed in three separate increments of 10 to 12 mL. Each increment was in contact with the resin bed for 2 minutes. A total volume of 33 mL was collected for analysis. This procedure was repeated an additional 2 times such that 3 separate aliquots containing 33 mL of solution were collected and analyzed for chloride content. The chloride content of the first 33 mL measured 47 mg while the second and third aliquots measured 0 and 2 mg. Since chloride breakthrough occurs at 28 mL for a 12 gram column (Table 5) and the resin chloride capacity is 49 mg/g of resin (Table 5), then approximately 1/12 of the chloride was recovered by this method.

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Since regeneration is an essential component in utilizing these resins for a carbon capture process, a second method of liberating the chloride by means of hot water was investigated. The previous process utilized a static type method in which the resin was in contact with a specific volume of hot water for 2 minutes. In the second method, after a 12 gram column of Amberjet 4400 was challenged with 38 mL of Key West seawater, the column was dynamically rinsed with 100 mL of 60 °C water and approximately 10 mL aliquots of the effluent were collected and analyzed for chloride content. Table 9 shows that 54.80 mg of chloride was removed from the column in the first 10.3 mL of effluent. The chloride content of subsequent aliquots decreases until a steady state appears to occur once a total of 40 mL of hot water has contacted the resin and been collected. Approximately 1.5 mg of chloride is collected in each of the subsequent 10 mL aliquot effluent samples collected and analyzed. These results suggested that chloride recovery would not be observed by further rinsing of the column with hot water. As a result after 72.2 mL of total effluent was collected and analyzed, it was determined that a total of 84.90 mg of chloride content was recovered from the column. Since the chloride capacity of the resin for this solution was 49 mg/g of resin (Table 5), then approximately 14% of the chloride was recovered from the column. This method proved to be considerably better than the previous effort to liberate chloride where only 8% of the chloride was recovered. The efficiency of CO_2 and chloride recovery from the resin column may further be increased by raising the temperature of the water and applying mixing and sonication to enhance mass transfer. However given the constraints of the processing times, hot water regeneration does not appear to be feasible.

Table 9 - Regeneration of Amberjet 4400 in OH Form Using 60 °C Deionized Water

Solution (mL)	Chloride (g/L)	Total Chloride (mg)
10.3	5.3	54.8
10.3	1.4	14.6
10.3	0.7	7.3
10.3	0.4	3.6
10.3	0.2	1.7
10.3	0.1	1.4
10.4	0.1	1.5
Total Solution	**Total Chloride (g/L)**	**Total Chloride (mg)**
72.2	8.2	84.9

4.4 Carbon Capture Feasibility Determination

It is estimated that 443,900 m³/day of carbon dioxide is needed for a synthetic hydrocarbon fuel process to produce 100,000 gal/day of jet fuel. The CO_2 capacity of the Amberjet resin given in Table 7 for seawater is 0.07 mg/g of resin. The amount of resin needed for such a process would be as follows:

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443,900 m^3/day CO_2 x 1.98 kg/m^3 x 1000 g/1 kg x 1000 mg/g x 1 day/24 hrs =

$$\textbf{3.7 x 10}^{\textbf{10}} \textbf{ mg/hrs of CO}_{\textbf{2}}$$

3.7 x 10^{10} mg/hrs of CO_2/0.07 mg CO_2/g resin =

$$\textbf{5.2 x 10}^{\textbf{11}} \textbf{ g of resin/hrs}$$

5.2 x 10^{11} g of resin/hrs x 1 x10^{-6} MT/gram =

$$\textbf{520,000 MT of resin/hrs or 8,700 MT of resin/min}$$

Thus 8700 MT of resin/min requires a 60 second processing time for both the extraction of CO_2 and regeneration of the resin. Though this amount of resin may be feasible for a land based process, it would not be for a process aboard an aircraft carrier size platform or a floating platform such as an OTEC ship. A strike group consumes 100,000 gal/day of JP5 and an additional 3.5 million gallons of fuel is stored.

$$3.5 \text{ x } 10^6 \text{ gal of JP5 x } 3.785 \text{ L/gal x } 0.8 \text{ g/mL x } 1000 \text{ mL/L} =$$

$$\textbf{1.1 x 10}^{\textbf{10}} \textbf{ grams of JP5 or 11,000 MT}$$

This is equivalent to 11,000 MT of ship displacement for a synthetic fuel process. If anion exchange resins are used for carbon capture, than only 2,300 MT of displacement is left for the rest of the process, which will include hydrogen generation equipment and pumps for water processing.

5.0 CONCLUSIONS

Strong base anion exchange resins were studied to determine if they could be used as a feasible and practical method for sequestering CO_2 from seawater. This direct approach captures bound CO_2 in the form of bicarbonate from seawater. CO_2 capacity, rate of exchange, and the effects of ionic strength were measured in initial static studies using simple model bicarbonate and bicarbonate/chloride systems. CO_2 exchange efficiencies in the presence of high concentrations of chloride were greatly improved by changing the operating conditions from a static mode to a dynamic flowing process. The results indicate that bicarbonate does compete with chloride even in conditions such as seawater where chloride concentrations are 240 times greater than that of bicarbonate. The disadvantage of operating strong base anion exchange resins in a seawater environment is the CO_2 capacity. The CO_2 resin capacity in Key West seawater measured 0.07 mg/gram of resin. To produce 100,000 gallons of fuel per day, it is estimated that 8,700 MT/min of resin is required for the process. In addition studies suggest it is difficult to regenerate the strong base anion exchange resins in the presence chloride anions without using a strong base such as sodium hydroxide. Though such a process may be feasible

for land based operations, the amount and weight of resin and method of regeneration would not be practical for sea-based applications.

6.0 RECOMMENDATIONS

Strong base anion exchange resins were determined to be impractical for sequestering large amounts of CO_2 from seawater for use as a carbon feedstock in a sea-based fuel production process. It is recommended that additional studies be conducted to determine the viability of other proven technologies for carbon capture.

Polypropylene microporous membranes in closed systems have proven to increase CO_2 recovery from seawater by the additional extraction of bound CO_2 in the form of bicarbonate [8,9]. In efforts to enhance CO_2 capture by this approach, commercial hollow fiber membrane contactors are proposed to be studied in a simulated open ocean environment. This type of system is not limited by a fixed volume. As a volume of seawater comes into contact with the membrane it will quickly be replenished by the ocean's current. This continuous cycle of seawater eliminates the opposing forces created by the re-equilibration of the seawater buffer system. Thus an increase in CO_2 sequestration should be possible.

Strong acid cation exchange resins are the indirect method of removing CO_2 from seawater. Studies have shown that the capacity and recovery rate for CO_2 by this method is practical for a sea-based fuel production process [7]. However, there is still a critical scientific issue that must further be addressed for use of this technology at sea. Regeneration of this material efficiently currently requires the use of strong acid. Developing an approach that uses electricity to produce protons for regeneration is a viable alternative that will require determining CO_2 capacities, regeneration efficiencies, and additional energy penalties for the regeneration process.

Given sufficient funding the microporous membrane contactor work could be completed in two man years, and the electrical regeneration work would require an additional two man years.

7.0 ACKNOWLEDGMENTS

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